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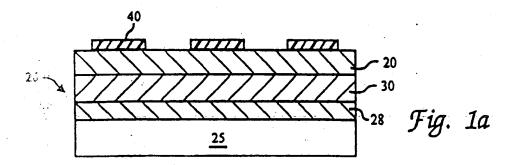
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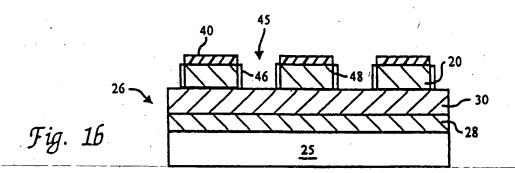
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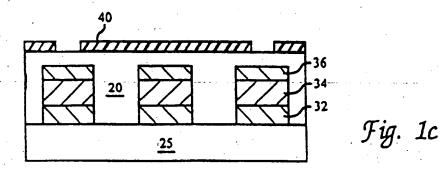
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- (54) Method of etching dielectric layer using a plasma generated from a mixture of flourohydrocarbon gas, NH3-genrating gas, and carbon-oxygen containing gas
- (57) A method of etching a dielectric layer on a substrate with high etching selectivity, low etch rate microloading, and high etch rates is described. In the method, a substrate having a dielectric layer with resist material thereon, is placed in a process zone, a process gas is introduced into the process zone, and a plasma is formed from the process gas to etch the dielectric layer on the substrate. The process gas comprises (i) fluoro-

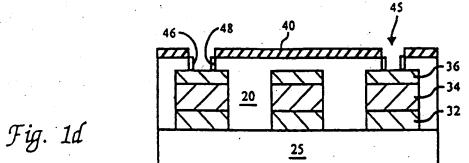
hydrocarbon gas for forming fluorine-containing etchant species capable of etching the dielectric layer, (ii) NH₃-generating gas having a liquefaction temperature L_T in a range of temperatures ΔT of from about -60°C to about 20°C, and (iii) oxycarbon gas containing carbon and oxygen bonded to one another. The temperature of substrate is maintained within about \pm 50°C of the liquefaction temperature L_T of the NH₃-generating gas.



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Description

The present invention relates to a process for etching substrates, and in particular, for etching dielectric layers, such as silicon dioxide, on semiconductor substrates.

In integrated circuit fabrication, it is often desirable to etch electrically insulative dielectric layers, such as silicon dioxide, undoped silicate glass, phosphosilicate glass (PSG), borophosphosilicate glass (BPSG), Si₃N₄, or TEOS deposited glass, that are used to electrically isolate devices or features formed on the substrate. For example, the dielectric layer can be deposited on a monocrystalline silicon substrate; a polysilicon layer on the substrate; or on anti-reflective or diffusion barrier layers, such as titanium silicide or titanium nitride. As another example, the dielectric layer can be deposited on electrically conductive interconnect lines that are used to electrically connect devices formed on semiconductor substrates. To etch the dielectric layer, resist material is deposited on the dielectric layer and patterned using photolithographic methods to the desired configuration of holes or lines. Holes are etched though the exposed portions of the insulative dielectric layers to the underlayers, such as silicon, polysilicon, titanium silicide, or titanium nitride layers. The etched holes are filled with electrically conductive material to form vertical electrically conductive interconnects, commonly known as contact holes or vias, which connect devices formed on the substrate or interconnect lower levels of interconnect lines to upper levels of interconnect lines.

In conventional etching processes, the dielectric layer is etched using a plasma of fluorocarbon gases, including for example, CHF3, CH3F, CF4, and CH2F2 For example, commonly assigned U.S. patent no. 5,242,538, which is incorporated herein by reference, discloses one preferred etchant gas composition comprising CH_3F , CF_4 , argon, and NH_3 . The NH_3 gas is used in an amount ranging from about 5 to 20%, and more preferably about 10%, by volume of the total gas flow, to serve as a source of hydrogen radicals in the etching process. However, such conventional gas compositions do not provide dielectric etch rates exceeding 700 to 900 nm/minute, and often do not allow simultaneous control of the etch rate, etching selectivity ratio, and etch profile angle. Tailoring the gas composition to provide high etch rates results in low ciching selectivity ratios and unacceptable etch profile angles, or vice versa. Modern integrated circuits often require etching selectivity ratios of greater than 10:1 with respect to the resist, and greater than 20:1 with respect to polysilicon, WSi, and TiSi, The etching selectivity ratio is the ratio of the dielectric etch rate to the rate of etching of the overlying resist layer, or the underlying silicon, polysilicon, titanium silicide, or titanium nitride layer. The etch profile angle, i. e., the angle between the sidewall of the etched feature and the plane of the substrate, is ideally about 90° to provide features having straight and substantially perpendicular sidewalls. However, conventional etching processes often provide profile angles of less than 85°.

Another problem with many conventional etching processes is that such processes can often only be operated in a narrow processing window, *i.e.*, in a narrow range of process conditions that provide adequate etching characteristics. It is generally desirable to have a more tolerant etching process that operates in a wider range of processing conditions to allow tailoring the process conditions to achieve particular combinations of etching rates and etching selectivity ratios for different types of materials on the substrate.

It is also desirable for the etchant gas to provide dissociated carbon species that form polymeric byproduct deposits, commonly known as "passivating" layers, on the sidewalls of freshly etched features, to limit etching of the sidewalls and provide "anisotropic" etching. However, excessive deposition of passivating layers on the sidewalls of the etched features is undesirable, and can result in lower dielectric etching rates, that typically range from about 250 to 300 nm/minute.

Thus, there is a need for an etching process that provides high etching rates and good etching selectivity ratios. It is also desirable for the etching process to provide uniform profile angles of at least about 85°. It is further desirable for the etching process to operate effectively in a wide range of process conditions to allow tailoring of process conditions for particular combinations of materials.

The present invention provides a method of etching a dielectric layer supported by a silicon wafer or other substrate and having a resist layer on portions thereof, at high etch rates, with good etching selectivity, and operable in a wide range of processing conditions. The method comprises the steps of placing the substrate and the dielectric layer supported thereon in a process zone, and forming a plasma from process gas introduced into the process zone to etch the dielectric layer on the substrate. The method is characterized in that the process gas comprises (i) fluorohydrocarbon gas for forming fluorine-containing etchant species, (ii) NH3generating gas having a liquefaction temperature LT from -60 to 20°C; and (iii) oxycarbon gas containing carbon and oxygen bonded to each other; and the substrate and the dielectric layer is maintained at a temperature (LT - 50)°C to (LT + 50)°C. It is believed that at least a portion of the NH₃-generating gas forms NH₃ chemical species that adhere to the substrate surface at the liquefaction temperatures to enhance the etching rate of the dielectric layer through surface reactions on the sub-

The etching process provided unexpectedly high dielectric etch rates up to about 900 nm/minute in combination with excellent etching selectivity ratios. The unexpected etching properties were obtained by maintaining the volumetric flow ratio of the fluorohydrocarbon to NH₃-generating gas within a range of about 2.5:1 to about 7:1. Furthermore, wide etching processing windows were obtained when carbon-oxygen gas was added. Preferably, the volumetric flow ratio of carbon-oxygen to fluorohydrocarbon gas was maintained at > 0.1: 1 and ≤ 1.1 .

A preferred etchant gas composition comprises (i) fluorohydrocarbon gas selected from the group consisting of CH₃F, CHF₃, C₂HF₅, and C₂H₂F₂, and more preferably CHF₃; and (ii) fluorocarbon gas selected from the group consisting of CF₄, C₂F₆, C₃F₈, C₄F₈, and C₄F₁₀, and more preferably CF₄. The NH₃-generating gas can comprise NH₃, NH₄OH, CH₃NH₂, C₂H₅NH₂, C₃H₈NH₂, and mixtures thereof, of which NH₃ is preferred. The carbon-oxygen gas can comprise CO, CO₂, HCOOH, HCOHO, CH₃COOH, CH₃OH, and mixtures thereof, of which CO is preferred. An inert gas, such as argon, capable of being activated by the plasma to sputter material from the substrate can also be added to the process gas to further enhance etch rates and provide anisotropic etching.

These and other features, aspects, and advantages of the present invention will be better understood from the following drawings, description and appended claims, which illustrate examples of the invention, where:

Figure 1a is a schematic in vertical cross-section of a dielectric layer povering a substrate;

Figure 1b is a schematic in vertical cross-section of the substrate of Figure Ia after etching of the dielectric layer showing substantially anisotropically etched contact holes;

Figure 1c is a schematic in vertical cross-section of a dielectric layer covering electrically conductive interconnection linus on a substrate;

Figure 1d is a schematic in vertical cross-section of the substrate of Figure 1c after etching of the dielectric layer showing substantially anisotropically etched vias;

Figure 2 is a settlematic view in vertical cross-section of a process of namber suitable for practicing the etching process of the present invention;

Figure 3 is a graph showing the change in silicon dioxide, resist, and polysilicon etch rates as a function of the volume tric flow ratio of CHF₃ to NH₃;

Figure 4 is a graph showing the change in silicon dioxide and pet, Histon etch rates for increasing flow rates of NH₃ graph.

Figure 5 is a graph showing the change in silicon dioxide and poly illicon etch rates as a function of the temperature of the support holding the substrate;

Figure 6 is a graph showing the change in profile angle for etched features as a function of the volumetric flow ratio of CHF₃ to NH₃; and

Figure 7 is a graph showing the change in silicon dioxide and polysilicon etch rates for increasing flow rates of CO gas.

The etching process of the present invention is useful for etching dielectric 20 on a substrate 25, as shown in Figures 1a - 1d, with high etching selectivity and good etch rates. The substrate 25 can be made of any material, such as glass, ceramic, metal, polymer, or semiconductor substrates, such as a silicon or gallium arsenide wafers. The dielectric 20 on the substrate 25 typically comprises a layer of silicon oxide, phosphosilicate glass (PSG), or borophosphosilicate glass (BPSG), having thickness of about 400 to 1500 nm. The dielectric layer 20 can also comprise plurality of layers, such as for example, a silicon oxide layer having a thickness of about 100 to 500 nm, covered by a 300 to 800 nm BPSG layer. The dielectric layer 20 is used to electrically isolate devices or interconnect lines formed on the substrate 25. For example, the dielectric layer 20 can be deposited on an underlayer 26, such as a doped polysilicon layer 28 or a diffusion layer 30, to electrically isolate the underlayer 26, as shown in Figure 1a. Dielectric layers 20 are also used to cover etched interconnect lines that include (i) a lower diffusion barrier layer 32, such as titanium, tungsten, titanium-tungsten or titanium nitride; (ii) an electrically conductive layer 34 comprising aluminum, copper and silicon; and (iii) an anti-reflective layer 36, such as silicon, titanium nitride or titanium-tungsten, as shown in Figure 1c, each of the layers being typically from about 200 nm to about 1000 nm thick. Although the etching method of the present invention is illustrated for etching of dielectric layers, the etching method can also be used to etch films which include non-oxide layers such as silicon, polysilicon, silicide, nitride, or boride layers, for example, Ta₂O₅, TiO₂, TiN, WSi_x, and MoSi_x. Thus, the present invention should not be limited to etching of dielectric layers.

Typically, a photoresist 40, such as "RISTON," manufactured by duPont de Nemours Chemical Company. is applied on the dielectric layer 20, to a thickness of about 0.4 to about 1.3 micron, and the features 45 to be etched in the insulative dielectric layer, such as contact holes or vias, are defined using conventional lithographic processes in which the resist is exposed to a pattern of light through a mask that corresponds to the desired configuration of features 45. The dielectric layer 20 underlying the unexposed portions of the resist are etched in the etching process. During the etching process, polymeric passivating deposits 46 are typically formed on the sidewalls 48 of the etched features 45. The etched features 45 are typically sized from about 0.2 to about 10 microns, and more typically about 0.4 to 2 microns, and the spacing between the features is typically from 0.2 microns to 10 microns.

In the present process, the dielectric layer 20 on the substrate 25 is etched in a process chamber 50, such as for example, an MxP OXIDE ETCH chamber, commercially available from Applied Materials Inc., Santa Clara, California, as shown in Figure 2, and generally described in commonly assigned U.S. patent nos. 4,842,683 to Cheng, et al., and 4,668,338 to Maydan, et al., both of which are incorporated herein by reference. The particular embodiment of the process chamber 50 shown herein, is suitable for processing of semiconductor substrates 25, is provided only to illustrate the invention, and abould not be used to limit the scope of the invention. For example, the etching process of ther? present invention can be used to etch any substrate 25, and can be used for manufacturing processes other than semiconductor labrication.

To perform the process, the chamber 50 is evacuated to a pressure of tess than about 1 mTorr, and a substrate 25 is transferred to a plasma zone 55 of the chamber 50 from a loan took transfer chamber (not shown) maintained at vacasta. Typically, the plasma zone 55 comprises a volumes of at least about 5,000 cm3, and more preferably (e. about 10,000 to about 50,000 cm³. The substrate 25 Page acced on a support that also serves as a cathode can incide 60, and the sidewalls of the chamber 50 are a charically grounded to form an anode electrode 65. Trac. 3. Instrate 25 an be held in place during the etching process using a mechanical or electrostatic chuck (nct area) with grooves in which a coolant gas, such as here s held to control the temperature of the substrate.

Process gas a introduced into the chamber 50 through a gas clist the substrate 25 a pressure rangir and more typicall, is maintained in the from the process. current to an 🖖 process changed current to the 🚑 the process chair pacitively. In re. 1 plasma is typic an RF voltage 3 about 2000 ₩:: electrically g tively, an RF c Watts to about coil to inductive generate the ; ... quency of the i trodes 60, 65 L Khz to about 3 MHz.

The plas cyclotron resfor 80 peripherally disposed about the chamber 50 is maintained at ⇒n about 1 to about 1000 mTorr, 11 10 to 300 mTorr. An electric field tasma zone 55 to form a plasma ii) inductively by applying an RF coil (not shown) encircling the ii) capacitively by applying an RF and anode electrodes 60, 65 in ി, or (iii) both inductively and caon etching (RIE) processes, the acitively generated by applying wer level of from about 100 to e cathode electrode 60, and by he anode electrode 65. Alternaa power level of from about 750 Hts can be applied to an inductor e energy into the chamber 50 to the plasma zone 55. The freant applied to the process elecor coil is typically from about 50 and more typically about 13.56

iso be enhanced using electron r magnetically enhanced reac-

tors, in which a magnetic field generator 85, such as a permanent magnet or electromagnetic coils, is used to apply a magnetic field in the plasma zone 55 to increase the density and uniformity of the plasma in the plasma zone 55. Preferably, the magnetic field comprises a rotating magnetic field with the axis of the field rotating parallel to the plane of the substrate 25, as described in U.S. Patent No. 4,842,683, issued June 27, 1989, which is incorporated herein by reference. The magnetic field in the chamber 50 should be sufficiently strong to increase the density of the ions formed in the plasma, and sufficiently uniform to reduce charge-up damage to features 45 such as CMOS gates. Generally, the magnetic field as measured on a surface of the substrate 25 is less than about 500 Gauss, more typically from about 10 to about 100 Gauss, and most typically from about 10 Gauss to about 60 Gauss.

Spent process gas and etchant byproducts are exhausted from the process chamber 50 through an exhaust system 90 capable of achieving a minimum pressure of about 10-3 Torr in the process chamber. A throttle valve 95 is provided in the exhaust for controlling the pressure in the chamber 50. Also, an optical endpoint measurement technique is typically used to determine completion of the etching process for a specific layer by measuring the change in light emission of a particular wavelength corresponding to a detectable gaseous species. A sudden decrease or increase in the amount of the detectable species, such as for example, CO or CN. that results from chemical reaction of the process gas with the silicon dioxide or polysilicon layer indicates completion of etching of the dielectric layer 20 and start of etching of the underlayer 26.

The etching process of the present invention uses a process gas that provides high etch rates and highly selective etching of the dielectric layers 20 on the substrate 25. The process gas includes (i) fluorohydro-carbon gas for forming fluorine-containing etchant species capable of etching the dielectric layer 20, and for forming passivating deposits 46 on the substrate 25, (ii) NH₃generating gas for enhancing etching rates of the fluorine-containing etchant species by adsorping onto the surface of the substrate, (iii) carbon-oxygen gas for allowing the etching process to operate in a wider range of processing conditions, and (iv) optionally, an inert gas can be added to the process gas to provide sputtering ions that sputter material from the substrate 25. In the etching process, the process gas is introduced into the chamber, and pressure in the chamber is maintained from about 10 to 500 mTorr, and more preferably from about 50 to about 300 mTorr. The RF power applied to the process electrodes 60, 65 is preferably from about 200 to about 2000 Watts, and more preferably from about 400 to about 1200 Watts. Preferred process gas compositions and volumetric flow ratios will now be described.

The fluorohydrocarbon gas is capable of forming fluorine-containing species that etch the dielectric layer **20** on the substrate 25. For example, a silicon dioxide layer is etched by the crine-containing ions and neutrals, such as F, HF, F-, CF, and CF₂ to form volatile SiF_x species that are exhausted from the chamber **50**. By fluor-ohydrocarbon gas it is meant a gas that includes carbon, fluorine, and hydrogen, preferred fluorohydrocarbon gases comprising, for example, CHF₃, CH₃F, C₂HF₅, CH₂F₂, and mixtures thereof. The NH₃-generating gas comprises ammonia or a gas capable of generating NH₃-containing species such as gases comprising NH₂-, NH₃, or NH₄-, it is or molecules, including for example NH₃, NH₄OF CH₃NH₂, C₂H₅NH₂, C₃H₈NH₂, and mixtures thereot. Ct these gases, NH₃ is preferred for the reasons provided below.

It has been discovered that fluorohydrocarbon gas in combination with NH3-generating gas provides unexpected and surprising results. Although the reaction mechanism is not fully understood it is believed that the following reaction rate hanism provides increased etch rates and higher et an a selectivity. The NH3-generating gas is selected to the value high sticking coefficient on the dielectric layer 20, of preferably at least about 0.3, and more preferably at least about 0.5. The higher sticking coefficient occurs because the NH₃-generating gas has a relatively high liquefaction temperature L_T (compared to that of conventional etchant gases) of at least about -80°C, and more programbly in a range of temperatures ΔT of from about to about 20°C. For example, whereas NHa has :upfaction temperature of -33°C and a sticking coant of about 0.5; a fluorocarbon gas, such as CF₃ > 5 a liquefaction temperature of about -100°C and a licking coefficient of less than about 0.1. The high a liquefaction temperatures and higher sticking coet. It ents are believed to cause at least a portion of gaseous and figuid NH3-generating phases, such as NH₃ or NH. ecies, to adsorb on the substrate rocess and react with fluorohy-25 during the clan imple CHF₃), on the surface of drocarbon gas (f. the substrate, but 'owing reactions:"

$$20HF_3 + 2F_3 \rightarrow NH_4HF_2 + 2CF_2$$
 (1)

$$2CHF_{+} + \cdots + NH_{A}F + HF + 2CF_{2}$$
 (2)

The chemical (1) HF, HF₂, and for results in rapid at the surface read to reactions in which limit reaction rated process gas specified products away for

During the a cooled to tenant NH₃-generation

The of the highly reactive NH₄F, less to the substrate surface 25 of the dielectric layer 20 because the much faster than gas transport welly slow transport mechanisms ring mass transport of etchant the substrate, and etchant bysobstrate.

corocess, the substrate 25 is sufficiently low to cause the to adsorb onto the surface of

the substrate 25. The substrate temperatures are actually the temperatures of the support 60 used to support the substrate, which are typically 5 to 50°C lower than the true substrate temperatures and are measured by a thermocouple located within the support. Preferably, the substrate 25 is cooled to temperatures that fall in a range of temperatures within about ± 50°C, and more preferably about \pm 30°C, of the liquefaction temperature L_T of the NH₃-generating gas to allow adsorbtion of the gas on the substrate surface. Thus, for liquefaction temperatures L_T within a range of temperatures ΔT of from about -60°C to about 20°C. The substrate is maintained at temperatures ranging from about -110°C to about 70°C, and more preferably from about -90°C to about 50°C. Most preferably, the substrate 25 is maintained at temperatures substantially equivalent to the liquefaction temperature L_T of the NH₃-generating gas.

One aspect of the unexpected results obtained from the present process are shown in Figure 3, which graphs etch rates obtained using a process gas comprising CHF₃ and NH₃. It is seen that the average etch rates of the dielectric, photoresist 40, and polysilicon layers, vary nonlinearly with increasing flow ratios of CHF3 to NH₃. The etch rate of silicon dioxide, rapidly increases at a CHF3:NH3 flow ratio of from 1:0 to about 2:1, as shown by the portion 202 of the curve 200. Thereafter, the silicon dioxide etch rate rapidly decreases as the CHF₃:NH₃ flow ratio increases from about 2:1 to about 2.5:1, as shown by the portion 204. Of particular interest is the portion 206 of the line 200, corresponding to CHF₃:NH₃ flow ratios of from about 2.5:1 to about 7:1, where the average etch rate of the silicon dioxide layer remains relatively uniform and stable for a relatively wide range of gas flow ratios.

The average polysilicon etch rates, as shown by line 210 in Figure 3, exhibits similar behavior with the polysilicon etch rate rapidly increasing for CHF₃ to NH₃ flow ratios of 0:1 to 2:1, as shown by the portion 212 of the line 210; and thereafter, rapidly decreasing for flow ratios of about 2:1 to about 3:1, as shown by the portion 214. At CHF₃:NH₃ flow ratios less than about 2:5:1, the high polysilicon etch rates results in excessive etching of the polysilicon layer, and etching selectivity ratios as low as 2:1. In contrast, for CHF₃ to NH₃ flow ratios of about 2.5:1 to about 7:1, the etch rate of polysilicon is low and relatively stable, as shown by the portion 216.

The resist etch rate, as shown by the line 220 of Figure 3, initially rapidly decreases for CHF₃:NH₃ flow ratios between 0:1 to 3:1, as shown by the portion 222, and thereafter, more gradually decreases to zero, as shown by the portion 226. Operation of the etching process in the portion 222, at low CHF₃:NH₃ flow ratios of less than 2.5:1, would provide narrow processing windows because the dielectric etch rates changes rapidly for small changes in process gas flow rates, and normal flow rate fluctuations would cause significant variability in etch rates between different process runs. Also, the high resist etching rates at these flow ratios can result

in resist faceting, and etching of the dielectric layer 20 below the resis

Figure 3 dc instrates that a fluorohydrocarbon to is flow ratios of from about 2.5:1 to NH₃-generating about 7:1, and mere preferably from 3:1 to 6:1, provides stable and high etah rates of at least about 400-500 nm/ minute, while sing transcously providing good etching selectivity ratios for siching of silicon dioxide relative to resist and polysilied a. These flow ratios correspond to the portion 206 of .5 SiO₂ etch rate line 200, the portion n etc arate line 210, and the portion 216 of the poly. 222 of the resih rate line 220. In these portions of the etching rate ! es, the low polysilicon and resist etch rates provide his taneously the dcatric etch rates are maintained at relatively high lev. resist etching n over a wide raprocessing win : strate the impnation in the at optimal etchin... is and etching selectivity ratios.

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Furth 1 istics of the mixture, tures 45 hydroca: :

etching selectivity ratios; while simul-Also, the dielectric polysilicon and remain relatively stable and uniform of gas flow ratios to provide a wide * The e unexpected results demon-ಾ of sing a CHF₃ and NH₃ combi-1 ad villumetric flow ratios to provide to Firmes 4 and 5, it is seen that the non-linearly as a function of --ger--rating gas, and the tempera-old: : the substrate (commonly reerature). Figure 4 shows that die cetch rates vary in the form -s' ed curve, with dielectric etch NH ow rates from 0 to 25 sccm,

JHa . ow rates from 25 to 50 sccm.

ich rates also peak at an NH₃

, although to a lesser degree.

1 U-shaped variation in etch

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rates the unexpected results

10: inge in average dielectric and . 102 3 6 : function of increasing sub-; is. on that while the etch rate of 9 decreases with increasing rate of the polysilicon layer, selectivity ratio, does not sigreasing temperatures. This as substrate temperature sigthing rates, and higher substrate d to slow down the rate of etch-20 during etching of thin die-G or silicon dioxide layers. apperature range can be used . .ing selectivity ratios, which Hie with increasing tempera-

ார். அய்யைவே etching character-:arbon and NH₃-generating gas . .. in profile angle of etched fea-* increasing flow ratio of fluororating gas, as shown in Figure

6. The profile angle of the etched features were measured using the average value of multiple measurements of etched contact holes having diameter of about 0.8 μ m, at both the center and edge of the wafer, using SEM (Scanning Electron Microscope) photographs of crosssections of the etched substrate 25. It was observed that at low flow ratios of CHF3:NH3, namely at flow ratios less than about 2.5:1, the profile angles of the etched features 45 are typically less than 80°, and often as low as 70°. Furthermore, CHF₃:NH₃ flow ratios higher than 5: 1 also provided low profile angles of less than about 75°. In contrast, CHF3:NH3 volumetric flow ratios ranging from 2.5:1 to 5:1 provided optimal profile angles typically ranging from about 80° to about 90°, arid more typically from about 85° to 90°.

For these reasons, the volumetric flow ratio of fluorohydrocarbon to NH3-generating gas is selected specifically for particular material combinations to provide (i) a dielectric etch rate of at least about 500 nm/minute, (ii) a dielectric to resist etching selectivity ratio of at least about 10:1, and more typically at from 100:1 to ∞:1, and (iii) a dielectric to underlayer etching selectivity ratio of at least about 25:1. The volumetric flow ratio of fluorohydrocarbon to NH3-generating gas can also be adjusted so that the etched features 45 have profile angles of at least about 85°. As described above, preferred volumetric flow ratios of fluorohydrocarbon to NH3-generating gas that provide high etch rates, good etching selectivity, and excellent profile angles, are from about 2.5: 1 to about 7:1, and more preferably are from 3:1 to about 6:1. Although, preferred ranges of volumetric flow ratios are described herein, it should be understood that the volumetric flow ratios can be tailored for different combinations of materials, and to achieve specific etching selectivities, etch rates, or etched feature geometries, for example aspect ratios or profile angles, without deviating from the scope of the present invention.

It is further discovered that the addition of oxycarbon gas or carbon-oxygen gas (by which it is meant a gas containing carbon and oxygen bonded to each other) to the process gas allows the etching process to operate in a wider range of processing conditions, such as process gas flow rates, pressures, temperatures, and RF power levels. Preferred oxycarbon or carbon-oxygen gases include CO, CO2, HCOOH, HCOHO, CH₃COOH, and CH₃OH. The oxycarbon or carbon-oxygen gas typically reacts with fluorine-containing species to form volatile COF2, thereby reducing the fluorine concentration in the process chamber 50 and consequently reducing the rate of etching of polysilicon to provide higher etching selectivity ratios. In addition, the carbon-oxygen gas enhances the formation of free carbon and CF2 species that react with other species, such as nitrogen, fluorine, and boron to form polymeric passivating deposits 46 on the sidewalls of the etched features 45 to provide anisotropic etching of the dielectric layer. However, excessively high flow rates of the carbon-oxygen gas can cause thick passivating deposits 46 to

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flow rate		nchieve desired e	tching char-

ting high dielectric etch rates

over a v. ക്ഷം conditions. Pro' is added to the process gas to provide → ⇒ etching through highly directions 1150 substrate 25 by charged inert gal. gized by the electric field in the cl at das also assists in sputter-; chais 46 on the sidewalls of ing-off t the frest √s <5 to reduce the thickness</p> of such is desirable for the inert gas to have to ation energies, so that the inert ga ir onized metastable states that pro reactions which promote dissoci s. Suitable inert gases include an on, and krypton, of which argon is inert gas is added to the process sired anisotropic etching levels & ciation of the process gas. Howev.; llow rates can cause excessive t on the substrate 25, resulting ching of the dielectric layer 20 u e charged argon ions also **enh**and the NH3 or NH4 species adsorbsubstrate 25 by ion bomisotropic etching characbardmo teristich te volumetric flow ratio of from about 0.1:1 to about inert g. 10:1, a m 1:1 to about 3:1.

acteristic

In a me present invention, the proces fure of (i) fluorohydrocarbon gas that are absent hydrogen to 358, C4F8 and C4F10. It has been to have a market market and the fluorohydrocarbon gas that are absent hydrogen to 358, C4F8 and C4F10. It has been to have a market market and the fluorohydrocarbon gas and

drocarbon and fluorocarbon gases provides optimum etch rates and etching selectivity ratios. Although the gas chemistry-is not fully understood, it is believed that the fluorohydrocarbon gas provides hydrogen species that combine with free fluorine radicals to form gaseous HF that is exhausted from the chamber 50 to increase the carbon available to form passivating deposits 46, and limiting the fluorine species available for etching the dielectric 20. In contrast, the fluorocarbon gas provides increased amounts of free fluorine that balances microloading effects. However, excessive amounts of fluorohydrocarbon gas provides etched features having tapered or sloped sidewalls because of the high carbon content that results in increased passivating deposits on the sidewalls of the features. A preferred combination of gases include a fluorocarbon such as CF4, and a fluorohydrocarbon such as CHF3, in a volumetric flow ratio of about 0:1 to about 1:2, and more preferably from about 0.1:1 to about 1:20.

One preferred composition of process gas suitable for etching silicon dioxide layers on a silicon substrate 25 with high selectivity, comprises CHF₃, NH₃, CO, CF₄, and argon. For the volume within the process chamber 50 described herein, (i) a suitable flow rate of fluorohydrocarbon gas, such as CHF3, is from about 5 to about 200 sccm, and more preferably from 10 to 100 sccm; (ii) a suitable flow rate of NH3-generating gas is from about 2 to about 50 sccm, and more preferably from about 4 to about 20 sccm; (iii) a suitable flow rate of CO is from about 0 to about 200 sccm, and more preferably from about 10 to about 100 sccm; (iv) a suitable flow rate of fluorocarbon gas, such as CF₄, is preferably from about 0 to about 40 sccm, and more preferably from about 2 to about 20 sccm; and (v) a suitable flow rate of inert gas, such as argon, is from about 5 to about 300 sccm. and more preferably from about 15 to about 200 sccm. Because flow rates are selected depending upon the volume of the chamber 50, the invention should not be limited to the flow rates recited herein.

EXAMPLES

The following illustrative examples of the present invention are shown to etch dielectric layers 20 on semiconductor substrates 25, with high etch rates, and high etching selectivity ratios. However, the apparatus and method of the present invention can be used in other applications as would be apparent to those skilled in the art, and the scope of the present invention should not be limited to the illustrative examples provided herein.

In these example, the substrates 25 comprised silicon wafers having a diameter of 200 mm (8 inch), and coated with different layers, such as polysilicon, conductivity enhancement layers, or diffusion barrier layers 32, as described below. In each experiment the substrate 25 was placed on the cathode 60 of an MxP OXIDE ETCH chamber 50, the chamber 50 was maintained at a pressure of from about 80 mTorr to about 250 mTorr.

50

Process			THE3 and NH3 was used. The
substra:			> temperatures ranging within
about ± 1			action temperature L _T of NH ₃
gas wh			using a flow of helium on the
backsid:			25 maintained at a pressure
of about			was generated in the plasma
zone 55 .	' '		voltage to the process elec-
trodes €	•		vel of about 1000 Watts. The
plasma	*1 .	1	applying a rotating magnetic
field of	1 -		the plasma zone 55 .
Sc ·			nc optical microscopy tech-
niques			sure the (i) etch rates of the
dielect:			ਾਂਬਪੁਰਾs, and (ii) etch rate uni-
formity	:'}		an culated by measuring the
depth ct	:	*.	hed in the wafers. The etch-
ing sel			culated from the ratio of the
etch rati			riyers 20 to the etch rate of
the TiS-			sst layers.
ano me			or or mayoro.
Examp			2
<u>LAUIT</u>			ŕ
T},	,		into demonstrate use of a
	Ţ		sohydrocarbon gas, NH ₃ -
proces	-1		
genera			gas, and inert gas. In this
exam			120 on the substrate 25 com-
prised	į		er naving a thickness of 1 to
2 μm, :			son underlayer 26 having a
thickne			The dielectric layer 20 was
etc hec	•		rester contact holes.
Α,			ring 40 sccm CHF ₃ , 11 sccm
NH ₃ , ⊺			com Ar was used. This gas
comp ^r			flow ratio of about 4:1.
The p			10 was maintained at 138
mTorr.			ined at a temperature of
-30°C			from the process gas by
apply			evel of about 1000 Watts
to the			process chamber 50, and
the pl			sing a rotating magnetic
field h			∵ dauss.
E١			the effectiveness of a
CHF ₃			1:1, which provided a sil-
icon o			ig 600 nm/minute. In ad-
dition.		4	for etching silicon diox-
ide ref			00:1 were obtained, and
etchir			on dioxide to photoresist
of ∞:1			so, etched profile angles
greate			d.
0			-
Exam			
Т			I to domanatesta the affect
			io demonstrate the effect
of a c			rohydrocarbon gas:NH ₃ -
gen er			strate use of fluorocarbon
gas. I.			ctric layer 20 comprised
bor on			(BPSG) having a thick-
ness (n underlayer 26 compris-
in a Tic			i,

ing Ti

71

cm NH₃, 11 sccm CF₄, and 80 sccm Ar. This gas composition had a CHF₃:NH₃ ratio of about 5:1. The pressure in the chamber 50 was maintained at 225 mTorr, and the support maintained at a temperature of -30°C. A plasma was formed from a process gas for applying a current at a power level of about 1000 Watts to the electrodes 60, 65 in the process chamber 50, and the plasma was enhanced using a rotating magnetic field having a strength of 38 Gauss.

Example 2 demonstrated the effectiveness of a CHF₃:NH₃ ratio of about 5:1 for etching of contact holes having a diameter of 0.4 µm in a BPSG layer. BPSG etching rates greater than 900 nm/minute were obtained, and the etching selectivity ratio of BPSG to TiS₂ was greater than 25:1. The etching process also provided average profile angles of greater than 86°.

Example 3

20

This example is provided to demonstrate the effect of a different flow ratio of fluorohydrocarbon gas:NH₃-generating gas, in a process gas comprising fluorocarbon gas. In this example, the substrate **25** comprised a dielectric layer **20** of silicon oxide in a thickness of 1.6 µm deposited on a titanium nitride layer having a thickness of 500 Å. Via holes having a diameter of about 0.4 µm were etched in the dielectric layer **20**.

A process gas comprising 33 sccm CHF $_3$, 11 sccm NH $_3$, 5 sccm CF $_4$, and 66 sccm Ar, was used. This gas composition provided a CHF $_3$:NH $_3$ flow ratio of about 3: 1, and a CHF $_3$:CF $_4$ flow ratio of about 6.6:1. The pressure in the chamber 50 was maintained at 138 mTorr, and the support maintained at a temperature of -30°C. A plasma was formed from a process gas by applying a current at a power level of about 1000 Watts to the electrodes 60, 65 in the process chamber 50, and the plasma was enhanced using a rotating magnetic field having a strength of 38 Gauss.

In example 3, the silicon dioxide dielectric layer was etched at etch rates greater than 900 nm/minute, and an etching selectivity ratio of silicon dioxide to TiN of greater than 30:1 was obtained. The etched features 45 had a profile angle of greater than 89°.

Example 4

This example is provided to demonstrate use of a process gas comprising fluorohydrocarbon gas, NH₃-generating gas, carbon-oxygen gas, fluorocarbon gas, and inert gas, to show the advantages of adding carbon-oxygen gas to the process gas.

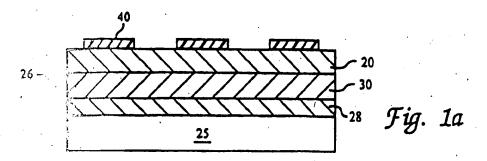
The process gas comprised 40 sccm CHF₃, 11 sccm NH₃, 40 sccm CO, 11 sccm CF₄, and 80 sccm Ar. This gas composition provided a CHF₃:NH₃ ratio of about 4:1, and a CO:CHF₃ ratio of about 1:1. The pressure in the chamber 50 was maintained at 138 mTorr, and the support maintained at a temperature of -30°C. A plasma was formed from a process gas by applying a

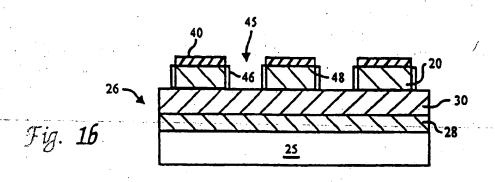
sed 55 sccm CHF₃, 11 sc-

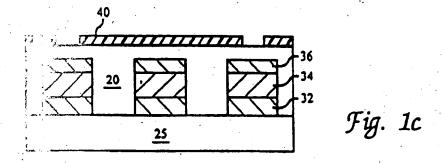
current :	bout 1000 Watts to the elec-			dielectric layer supported thereon in a process
trodes ·	chamber 50, and the plas-			zone, and forming a plasma from process gas intro-
ma wa:	Hating magnetic field having			duced into the process zone to etch the dielectric
a stren.				layer on the substrate;
This	d an etching selectivity ratio			characterized in that:
of etching in the	olysilicon of ∞:1, which is a			·
significant of	or conventional processes.			(1) the process gas comprises (i) fluorohydro-
In add 1. II.	th rates of greater than 600			carbon gas for forming fluorine-containing
nm/mi:	The extremely high polysili-			etchant species, (ii) NH ₃ -generating gas having
con et.	m combination with high sil-			a liquefaction temperature L _T from -60 to 20°C;
icon c	ovides a large process win-			and (iii) oxycarbon gas containing carbon and
dow fo	trate 25 in a range of differ-			oxygen bonded to each other; and
ent pro	out significantly reducing the			(2) the substrate and the dielectric layer is
etching	exide layer. This is a partic-			
ularly t.	ing the gas composition for	15		maintained at a temperature (L _T -50)°C to (L _T +
hig hly	different material combina-	,,,		50)°C.
-	unerent material combina-		_	'A
tions a	Color and addition of the state of		2.	A method according to claim 1 characterized in that
T) ··	s to an etching process that			
USOS &	and process conditions to			 the NH₃-generating gas is one or more of
obtain	s of up to 900 nm/minute	20		NH_3 , NH_4OH , CH_3NH_2 , $C_2H_5NH_2$, and
(900 0	electivity ratios exceeding			C ₃ H ₈ NH ₂ ;
100:1,	:1; and etching profile an-			(2) the fluorohydrocarbon gas is one or more of
gles h	been discovered that the			CHF ₃ , CH ₃ F, C ₂ HF ₅ , and C ₂ H ₂ F ₂ , and
com bi	carbon and NH ₃ -generat-			(3) the oxycarbon gas is one or more of CO,
ing ga	NH ₃ , provide excellent di-	25		CO ₂ , HCOOH, CH ₃ COOH, and CH ₃ OH.
electri	acrificing the etching selec-			
tivity	con. It has further been dis-		3.	A method according to claims 1 or 2 characterized
cover	and polysilicon etch rates			in that the volumetric flow ratio of:
cha nc	d curve for increasing flow			
ratios	NH ₃ -generating gas, and	30		(1) fluorohydrocarbon gas to NH ₃ -generating
at pre*	ing from about 2.5:1 to 7:1			gas is from 2.5:1 to 7:1; and
provid	tric etch rates and etching			(2) oxycarbon gas to fluorohydrocarbon gas is
selec:	n of carbon-oxygen gas to			
the flu				from 0.1 to 1:1.
	:13-generating process gas	25		A month and according to the control of the
provid	adows, by providing high di-	35	4.	and the same processing
electr	e of processing conditions,			claims characterized in that the process gas further
withor	ectivity ratios. The unusual			comprises a fluorocarbon gas which is one or more
adv a:	is combination of process			of CF_4 , C_2F_6 , C_3F_8 , C_4F_8 , and C_4F_{10} .
gas is	ed by the prior art, and re-		_	
sul ts i	ents in the field of etching	40	5.	A method according to claim 4 characterized in that
die lec				the fluorohydrocarbon gas is CHF ₃ , the fluorocar-
Α	ention has been described			bon gas is CF ₄ , and the volumetric flow ratio of CF ₄
in cor	gard to the preferred ver-			to CHF ₃ is less than about 1:2.
sio ns	are possible. For example,			
gase;	or composition to the fluor-	45	6.	A method according to any one of the preceding
ohy d:	erating gas, or carbon-oxy-			claims characterized in that the process gas further
gen ç	d the etching process can			comprises an inert gas which is one or more of ar-
be us	rials, such as for example		*	gon, xenon, neon, krypton, or helium; and the vol-
silicid	d carbides. Therefore, the			umetric flow ratio of inert gas to fluorohydrocarbon
appe:	e limited to the description	50		gas is from 1:1 to 3:1.
of the	ained herein.			g
			7.	A method of etching a dielectric layer supported by
			••	a silicon wafer or other substrate, the method com-
Claim				prising the steps of placing the substrate and the
		55		
1. A	folectric layer supported by			dielectric layer supported thereon in a process
a a	abstrate, the method com-			zone, and forming a plasma from process gas intro-
	•			duced into the process zone to etch the dielectric
P	ing the substrate and the			layer on the substrate;
				•

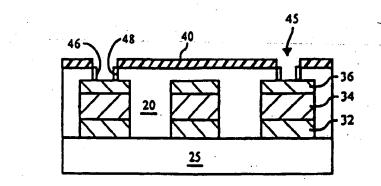
8. A r faccording to claim 7 characterized in that the trate and dielectric layer thereon is maintain that the characterizes from -110°C to 70°C.
9. A r recording to claim 7 or 8 characterized in that that characterized in the characterized in the characteric flow ratio of

 $F_3 \cap NH_3$ is from 2.5:1 to 7:1; O to CHF $_3$ is from 0.1:1 to 1:1; and $F_4 \mapsto CHF_3$ is from 0:1 to 1:2.

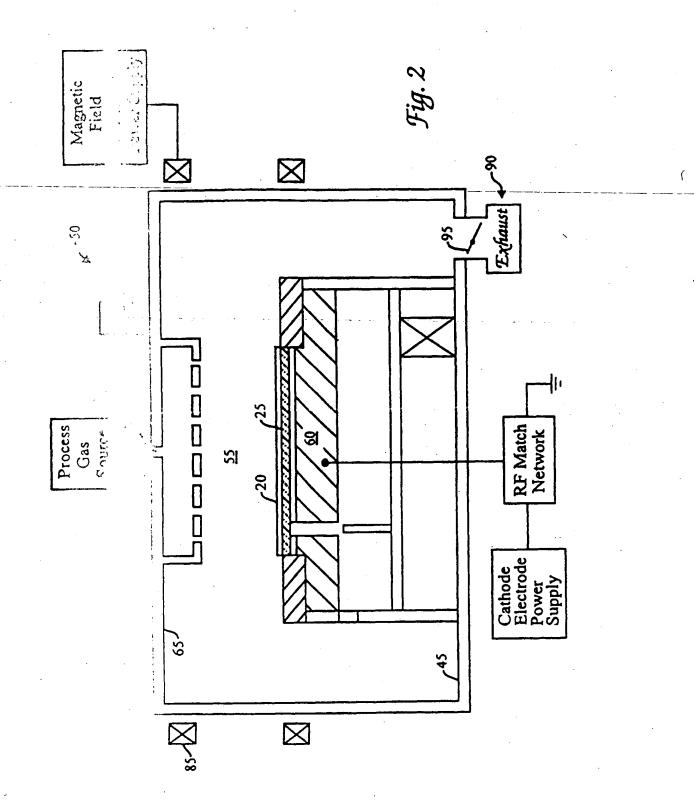








5 7. 1d



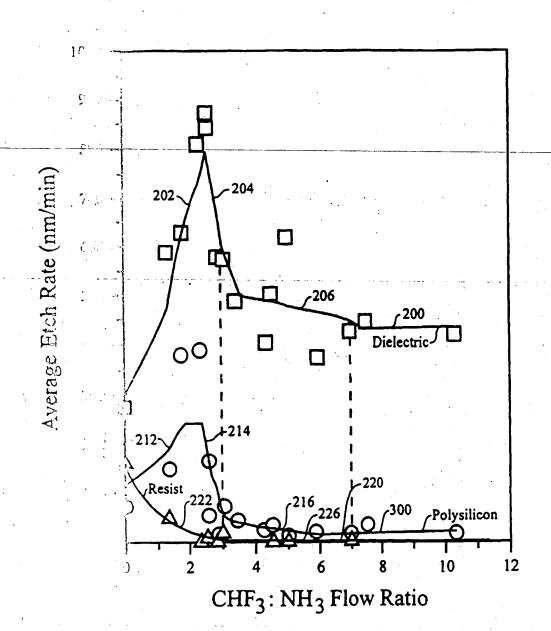
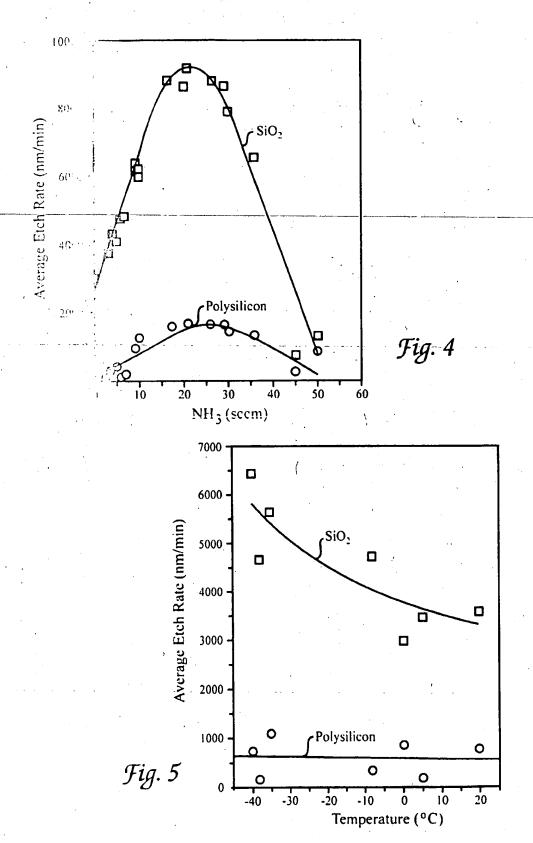
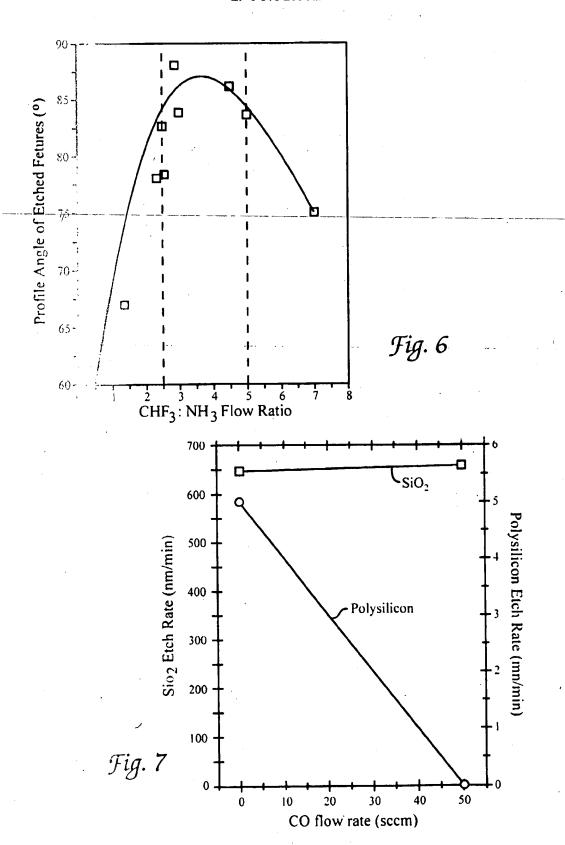


Fig. 3





DERWENT-ACC-NO: 1998-035216

DERWENT-WEEK: 199846

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TITLE: Etching dielectric layers at high etch rates, high selectivity ratios etc. - using plasmy formed from mixture of fluoro-hydrocarbon, ammonia-gen

erating, oxy:carkers and optionally <u>fluorocarbon</u> and inert gases

INVENTOR: DING, 'C; SHAN, H; WELCH, M; DING, J

PATENT-ASSIGNED: APPLIED MATERIALS INC[MATEN]

PRIORITY-DATA: 47 3GUS-0660966 (June 12, 1996), 1996US-0639388 (April 29, 1996)

PATENT-FAMILY:

PUB-NO PUB-DATE LANGUAGE **PAGES** MAIN-IPC Ε 016 H01L 021/311 **EP 81323**3 A2 H01L 021/3065 N/A 012 JP 10056001 A February **24, 1998** N/A 000 US 5814563 A ig tamber 29, 1998.

H01L 021/302

DESIGNATED-STATES: AT BEIGH DE DKIES FIFRIGBIGRIE IT LI LU MCINL PTISE

CITED-DOCUMER : No-SR.Pub

APPLICATIO -DATE :

AP. UESCRIPTOR APPL-NO APPL-DATE PUB-NO **EP 81323**3A2 1997EP-0304035 June 10, 1997 JP10056001A 1997JP-0147995 June 5, 1997 1996US-0639388 April 29, 1996 US 5814563 \ of 1996US-0660966 June 12, 1996 **US 58145**63A

.1/302; H01L021/3065; H01L021/311; H01L021/768 INT-CL (IPC): 1101

RELATED-ACC-N .37**-538384**

O: EP 813233A ABSTRACTED-PUT BASIC-ABSTRIAC nethod of etching a dielectric layer supported by a silicon te comprises: (a) placing the substrate supporting the wafer or other an dielectric layer in ncess zone; (b) etching the dielectric layer using a rocess gas comprising (i) fluoro-hydro carbon gas for plasma for: forming fluc 19.49 ing etchant species; (ii) ammonia-generating gas having a liquefaction ten

ture LT of -60 to 20 deg. C; and (iii) oxycarbon gas; and dielectric layer are maintained at (LT-50) deg. C to and (c) the substr (LT+50) deg. ○.

con oxide, the process can be used to etch, e.g. USE - In adu silicides, L ... les, and carbides. The process is useful in semicond : and circuit fabrication to electrically isolate devices or features for: substrate (e.g. monocrystalline silicon, polysilicon diffusion barrier layers, e.g. titanium silicide or layers, antietching holes between interconnect lines, the holes titanium nitili (2);

01/31/2002, EAST Version: 1.02.0008

being subsectionally filled with electrically conductive material to form (holes or vias) to connect devices formed on the vertical inter substrate or annect lower levels of interconnect lines to upper levels of interconna ADVANTAGE igh etching selectivity ratios of etching silicon oxide to polysilicon, $e_{\rm col} > 100$:1, etching profile angles higher than 85 deg. , and h rates of 600-900 nm/minute (9000 Angstrom /minute), silicon oxide providing lar ssing windows under a range of different process conditions. ABSTRACTE" O: US 5814563A **EQUIVALEN** ...STRACTS: A method of etching a dielectric layer supported by a the substrate comprises: (a) placing the substratesilicon waferelectric layer in a process zone; (b) etching the dielectric supporting the me formed from a process gas comprising (i) fluoro-hydro layer using a carbon gas f n a fluorine-containing etchant species; (ii) ammonia-ge: gas having a liquefaction temperature LT of -60 to 20 deg gas; and (c) the substrate and dielectric layer are C; and (iii) oxmaintained a deg. C to (LT+50) deg. C. USE - In add Distriction oxide, the process can be used to etch, e.g. silicides, box at ides, and carbides. The process is useful in semiconduc. extrated circuit fabrication to electrically isolate devices or features form substrate (e.g. monocrystalline silicon, polysilicon layers, anti-r or diffusion barrier layers, e.g. titanium silicide or titanium nitri etching holes between interconnect lines, the holes being subsect ed with electrically conductive material to form ic (holes or vias) to connect devices formed on the vertical inter. substrate or nnect lower levels of interconnect lines to upper levels of interconn-**ADVANTAGF** ching selectivity ratios of etching silicon oxide to 1, etching profile angles higher than 85 deg., and polysilicon, e silicon oxide s of 600-900 nm/minute (9000 Angstrom /minute), providing lar ising windows under a range of different process conditions. **CHOSEN-DR** ⊋wg.0/7 TITLE-TERM' **ETCH DIELE** YER HIGH <u>ETCH</u> RATE HIGH SELECT RATIO PLASMA FORMING MIXTURE **FLUORO HY** ON AMMONIA GENERATE OXY CARBON OPTION FLUOROCARBON **INERT GAS** ADDL-INDEX: **EVIAS SILICIDE BORIDE NITRIDE CARBIDE INTERCONN DERWENT-C** 3 U11 CPI-CODES: EPI-CODES: -3; U11-C07A1; U11-C07C3; U11-C08A5; UNLINKED-C REGISTRY-NUMBERS: 0246U; 0247U; 0270U; 0330U; 0341U; 0367U

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; 0378U ; 0814 U ; 1403U ; 1423U ; 1534U ; 1671U ; 1713U

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sion Numbers: C1998-011949 cession Numbers: N1998-028283

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